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Short-Term Effect of Lime, Phosphorus, and Iron Amendments on Water-Extractable Lead and Arsenic in Orchard Soils

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Abstract: Lead arsenate was extensively used to control insects in apple and plum orchards in the 1900s. Continuous use of lead arsenate resulted in elevated soil levels of lead (Pb) and arsenic (As). There are concerns that As and Pb will become solubilized upon a change in land use. *In situ* chemical stabilization practices, such as the use of phosphate-phosphorus (P), have been investigated as a possible method for reducing the solubility, mobility, and potential toxicity of Pb and As in these soils. The objective of this study was to determine the effectiveness of calcium carbonate (lime), P, and iron (Fe) amendments in reducing the solubility of As and Pb in lead-arsenate-treated soils over time. Under controlled conditions, two orchard soils, Thurmont loam (Hapludults) and Burch loam (Haploxerolls), were amended with reagent-grade calcium carbonate ($CaCO_3$), iron hydroxide [$Fe(OH)_3$], and potassium phosphate (KH_2PO_4) and incubated for 16 weeks at 26°C. The experimental results suggested that the inorganic P increased competitive sorption between $H_2PO_4^-$ and dihydrogen arsenate ($H_2AsO_4^-$), resulting in greater desorption of As in both Thurmont and Burch soils. Therefore, addition of lime, potassium phosphate, and Fe to lead-arsenate-contaminated soils could increase the risk of loss of soluble As and Pb from surface soil and potentially increase these metal species in runoff and movement to groundwater.

Keywords: Lead arsenate, soil amendments lime, water-extractable As, water-extractable Pb, phosphorus, and iron oxyhydroxide

INTRODUCTION

For many years, lead arsenate [$Pb_5OH(AsO_4)_3$] was the preferred insecticide used by farmers to control insects in orchards because it adhered to plant surfaces, thereby providing a long-lasting pesticidal effect (Shepard 1951; Peryea 1998; Vaneman, Murray, and Baker 1983). Lead (Pb) and arsenic (As) accumulated in the surface of orchard soils because Pb and As are not required by plants and are slightly sorbed onto clays, organic matter, and oxides of iron (Fe), aluminum (Al), and manganese (Mn) in soils (Aten et al. 1980; Peryea 1991; Wauchope 1975; Woolson, Axley, and Kearney 1971; Xu, Allard, and Grimvall 1991). Arsenic, being an anion (AsO_4^{3-}), is more mobile than Pb and moves in soil to a greater extend than Pb (Elfving et al. 1994; Peryea and Creger 1995). Keeping lead-arsenate-treated soil in orchard production effectively limits human exposure to Pb and As, because these metals do not accumulate in the fruits, but conversion of these lands from orchards to other land uses, such as vegetable crop production or residential development, enhances the likelihood of human exposure to residual Pb and As (Peryea 1989; USEPA 2003).

Phosphate

In situ chemical stabilization is one of the methods being considered for remediating lead-arsenate treated-soils (Nriagu 1974; Chaney and Ryan 1994). Application of phosphate to Pb contaminated soil was very effective in reducing Pb solubility. Hydroxyapatite [$Ca_5(PO_4)_3OH$] reduced initial soil solution Pb concentrations of $5-500$ mg L^{-1} to $0.18-19.7$ μg L^{-1} when combined with lead nitrate [$Pb(NO_3)_2$] solution (Ma et al. 1993). Aqueous Pb in Pb-contaminated soil was also reduced from 2273 to 36 μg L^{-1} with $Ca_5(PO_4)_3OH$ (Ma et al. 1993). Phosphate application to lead-arsenate-treated soils also reduced Pb solubility through the formation of insoluble lead phosphate (i.e., pyromorphite). However, there are concerns that such P application may increase As solubility, because phosphate and arsenate exhibit similar physicochemical behavior in soils and phosphate is adsorbed more readily than arsenate onto soil and organic matter surfaces, which could promote As leaching (Davenport and Peryea 1991; Kalbasi et al. 1995; Ruby, Davis, and Nicholson 1994; Peryea and Kammereck 1997).

Iron

Iron application to P-amended orchard soils could reduce solubilization of soil As induced by P application (Chaney et al. 1997). Iron oxyhydroxide had a high adsorption capacity for As (V); therefore, Fe could be very effective in immobilizing As. Woolson (1972) reported that As could be

fixed in soil in unavailable forms such as Fe arsenate. The degree of fixation, however, varies with time and among soils (Marin, Masschelyn, and Patrick 1992).

Lime

It has long been known that metals such as Pb or Fe are more soluble under acidic conditions. Moore (1985) found that soil Pb could be solubilized by acid rain. However, results of research on the use of lime to reduce Pb solubility are mixed. Turpeinen, Salminen, and Kairesalo (2000) observed no reduction in Pb solubility with the addition of lime, but others demonstrated that lime addition to Pb-contaminated soils reduced Pb solubility and uptake by plants (John and Van Learhoven 1972; Cox and Rains 1972; Hardiman, Banin, and Jacoby 1984; Bassuk 1986). Because the loss of agricultural lands to urbanization is occurring at an increasing rate in or near large metropolitan areas, improved understanding of the effects of soil additives to minimize the residual effects of past pest control practices is needed. The objectives of this study were to determine the effectiveness of calcium carbonate, phosphorus, and iron amendments in reducing the solubility of As and Pb in lead arsenate contaminated soils over time and to elucidate the mechanisms of solubilization to improve *in situ* mitigation practices.

MATERALS AND METHODS

Soil Collection and Selected Characteristics

Soils were collected from two orchards with a long history of lead arsenate application. One was a Thurmont loam (Oxyaquic Hapludults) from Washington County, MD, and the other was a Burch loam (Aridic Haploxerolls) from Chelan County, WA. The soils were stored in plastic buckets at field water content until use. Soil textural properties were determined using the hydrometer method (Gee and Bauder 1986). Soil pH was determined in a 1:1 soil–water suspension after 1 h of equilibrium. Electrical conductivity (EC) was measured in 1:2 soil–water suspensions after 1 h of equilibration. A carbon–nitrogen–hydrogen analyzer (Elementar Analysensysteme, Hanau, Germany) was used to determined organic carbon content of the soils. Water-extractable metals were determined by shaking 5 g of soil (dry-weight basis) with 20 mL of deionized water for 4 h, then centrifuging at 10,000 rpm for 5 min. The supernatant was filtered using Whatman No. 42 filter paper. For the Mehlich 1 extraction, 2 g of soil was shaken with 20 mL of Mehlich 1 solution for 5 min and filtered through a Whatman # 42 filter paper (Kuo 1996). Aluminum, calcium (Ca), Fe, Pb, Mn, and P concentrations in the extracts were determined using inductive coupled plasma-optical

Emission Spectroscopy with yttrium as internal standard. Arsenic concentration was determined using an ICP-OES with a modified hydride method in which 2 ml of the Mehlich 1 soil extract was placed in a 10-mL volumetric flask and 1.5 mL of concentrated hydrochloric acid (HCl) and 2 mL of a reducing solution containing 5% potassium iodine and 5% ascorbic acid were added and brought to volume with Mehlich 1 solution. Contents of the flask were mixed and allowed to stand for 30 min for the reduction of As(V) to As(III) to occur. A solution containing 0.5% sodium borohydride and 0.05% sodium hydroxide was used as the carrier solution in the ICP for the hydride generation (Chan and Sadana 1992).

Treatments

There were eight soil-amendment treatments: 1) $(-\text{lime} - \text{P} - \text{Fe})$; 2) $(-\text{lime} - \text{P} + 1\% \text{ Fe})$; 3) $(-\text{lime } - \text{Fe} + 1\% \text{ P})$; 4) $(-\text{lime } +1\% \text{ Fe} + 1\% \text{ P})$; 5) $(+\text{lime} - \text{ Fe} - \text{ P})$; 6. $(+\text{lime} - \text{P} + 1\% \text{ Fe})$; 7. $(+\text{lime} - \text{Fe} +1\% \text{ P})$; and 8) $(+\text{lime} +1\% \text{ Fe} + 1\% \text{ P})$. The iron hydroxide $[Fe(OH)_3]$ used in this experiment was prepared fresh by combining a 0.45 M solution of Ferric Nitrate $[Fe(NO_3)_3]$ with a 1.6 M sodium hydroxide (NaOH) solution at the rate of 1:3 (v/v). The precipitate was washed several times with deionized water until an EC value of 2.0 mS cm^{-1} was reached.

Calcium carbonate ($CaCO_3$) was added at the rate of 1.0 and 1.5 g kg^{-1} to the Thurmont and the Burch soils respectively. Phosphorus was added as monopotassium phosphate (KH_2PO_4) at the rate of 43.9 g kg^{-1} soil and the $Fe(OH)_3$ was weighed wet and added to bulk soil samples at rate of 200 g Kg^{-1} to provide 1% Fe in the soils. Field moist soils (900 g of oven-dry weight) and appropriate amounts of amendments were mixed, and deionized water was added to attain soil water contents of 0.183 and 0.34 g g^{-1}, equivalent to field capacity for the Burch and Thurmont soils, respectively. Each soil treatment was replicated three times and placed in 30×45 cm polyethylene bags. The amended soil in each bag was incubated at 26°C for 16 weeks in a constant-temperature chamber. The soil water content in each bag was maintained by weighing and adding deionized water if needed, taking into account the soil that was periodically removed for analysis. Soil samples (15 g) were removed at 2, 4, 6, 8, 10, and 16 weeks for pH, EC, and water-extractable As, Fe, Pb, and P determinations. The analysis of variance (ANOVA) procedure of the Statistical Analysis System was used to determine statistical significance of the soil-amendment treatments (SAS Institute 2000). Separation of means was done by Duncan's multiple range test at the 0.05 level of probability (Steel and Torrie 1980).

RESULTS AND DISCUSSION

Selected physical and chemical characteristics of the soils used are presented in Table 1. Soil pH was lower in the Thurmont than in the Burch soil. Organic

Table 1. Characteristics of orchard soils used in incubation experiment

Perimeters	Thurmont	Burch
Soil texture	Sandy loam	Sandy loam
Organic carbon (g kg^{-1})	69	8.3
pH	4.7	5.9
EC (mS cm^{-1})	2.5	0.18
Aluminum (mg kg^{-1})	2.6	6.2
Arsenic (mg kg^{-1})[a]	0.96	1.6
Arsenic (mg kg^{-1})	13.5	13.2
Calcium (mg kg^{-1})	680	31.2
Copper (mg kg^{-1})	5.9	2.4
Iron (mg kg^{-1})	64.4	231.3
Lead (mg kg^{-1})[a]	0.34	2.7
Lead (mg kg^{-1})	212	116
Manganese (mg kg^{-1})	79	41
Phosphorus (mg kg^{-1})	111	83

Note. Mehlich 1 extractable were used for all other elements.
[a]Water extractable.

carbon in the Thurmont soil was eight times greater than that of the Burch soil, which could provide a greater buffering capacity.

Although no difference in Mehlich 1–extractable As was observed between the two soils, water-extractable As and Pb concentrations were higher in the Burch soil than in the Thurmont soil prior to the experiment (Table 1). In addition, Mehlich 1–extractable Al and Fe concentrations were higher in the Burch soil.

Soil pH and EC

In most cases in the unlimed Thurmont and Burch soils, addition of $H_2PO_4^+$ and $Fe(OH)_3$ resulted in a higher soil pH than that in the control (Table 2). However, in the limed Burch soil treatment, addition of P alone significantly reduced soil pH throughout the incubation. A similar reduction in pH with P application was observed by Peryea (1989) when monoammonium phosphate and monocalcium phosphate were added to soils with pH values greater than 6.0.

In all cases, P application significantly increased EC value in both soils, but in most cases the values decreased over incubation time (Table 3). There were only slight differences observed in EC values among treatments with the addition of lime. The higher EC values observed with the (+P) treatment may have resulted from the potassium ion (K^+) added as potassium phosphate (Peryea 1989; McLean 1982).

Table 2. pH means and standard deviation of orchard soils amended with lime, iron and phosphate

Treatments	Sampling time (weeks)					
	2	4	6	8	10	16
Thurmont soil						
−L − Fe − P	4.61 ± 0.13d[a]	4.64 ± 0.01g	4.69 ± 0.15f	4.25 ± 0.02g	4.15 ± 0.01g	4.26 ± 0.01h
−L + Fe	4.92 ± 0.06c	4.75 ± 0.10f	4.85 ± 0.04e	4.46 ± 0.03f	4.38 ± 0.22f	4.60 ± 0.01g
−L + P	4.77 ± 0.00d	4.91 ± 0.02e	5.28 ± 0.01d	5.03 ± 0.02d	5.17 ± 0.04d	5.41 ± 0.01d
−L + Fe + P	5.33 ± 0.06b	5.49 ± 0.01c	5.69 ± 0.03b	5.45 ± 0.01b	5.51 ± 0.04b	5.69 ± 0.01b
+L − Fe − P	5.64 ± 0.06a	5.68 ± 0.03b	5.24 ± 0.02d	4.96 ± 0.02e	4.97 ± 0.02e	5.02 ± 0.01f
+L + Fe	5.74 ± 0.03a	5.76 ± 0.01a	5.44 ± 0.06c	5.19 ± 0.02c	5.19 ± 0.01d	5.28 ± 0.02e
+L + P	4.99 ± 0.04c	5.16 ± 0.01d	5.47 ± 0.01c	5.27 ± 0.01c	5.34 ± 0.02c	5.60 ± 0.01c
+L + Fe + P	5.67 ± 0.06a	5.71 ± 0.02ab	5.90 ± 0.05a	5.66 ± 0.04a	5.76 ± 0.04a	5.94 ± 0.02a
Burch Soil						
−L − Fe − P	5.92 ± 0.03f	5.35 ± 0.01f	5.23 ± 0.05e	5.03 ± 0.01h	5.11 ± 0.07d	5.07 ± 0.01f
−L + Fe	6.39 ± 0.08e	6.09 ± 0.07d	5.75 ± 0.06d	5.59 ± 0.02g	5.47 ± 0.14c	5.63 ± 0.01e
−L + P	5.56 ± 0.06g	5.69 ± 0.10e	5.96 ± 0.01c	5.69 ± 0.02f	5.79 ± 0.01bc	6.13 ± 0.03d
−L + Fe + P	6.61 ± 0.02d	6.72 ± 0.02c	6.80 ± 0.04b	6.60 ± 0.04d	6.67 ± 0.10a	6.85 ± 0.03c
+L − Fe − P	7.05 ± 0.16b	6.96 ± 0.22b	6.74 ± 0.20b	6.67 ± 0.04c	6.58 ± 0.01a	6.84 ± 0.07c
+L + Fe	7.42 ± 0.07a	7.19 ± 0.16a	7.03 ± 0.16a	6.85 ± 0.02a	6.47 ± 0.55a	7.10 ± 0.03a
+L +P	5.85 ± 0.03f	5.85 ± 0.03e	6.04 ± 0.02c	5.78 ± 0.01e	5.87 ± 0.01b	6.09 ± 0.01d
+L + Fe + P	6.82 ± 0.04c	6.89 ± 0.01bc	6.99 ± 0.01a	6.76 ± 0.02b	6.80 ± 0.02a	6.99 ± 0.01b

[a]Within columns for each soil, means with a letter in common are not significantly different at the p < 0.05 level.

Table 3. Electrical conductivity means (mS/cm) and standard deviation of orchard soils amended with lime, iron, and phosphate

| Treatments	Sampling time (weeks)					
	2	4	6	8	10	16
Thurmont soil						
−L − Fe − P	2.21 ± 0.03cd[a]	2.18 ± 0.18e	1.87 ± 0.13f	2.30 ± 0.01f	2.15 ± 0.11e	2.51 ± 0.17d
− L + Fe	2.10 ± 0.02d	1.87 ± 0.11f	1.80 ± 0.08f	2.26 ± 0.16f	2.03 ± 0.06e	2.34 ± 0.14de
−L + P	6.84 ± 0.07a	5.96 ± 0.26a	5.03 ± 0.07b	5.89 ± 0.04a	4.97 ± 0.33b	5.19 ± 0.07b
− L + Fe + P	4.77 ± 0.10b	4.01 ± 0.19d	4.04 ± 0.10d	4.39 ± 0.13c	4.06 ± 0.11c	3.97 ± 0.13c
+L − Fe − P	2.26 ± 0.01c	2.21 ± 0.03e	2.06 ± 0.04e	2.71 ± 0.05e	2.52 ± 0.07d	2.51 ± 0.06d
+L + Fe	2.10 ± 0.01d	2.01 ± 0.04e	2.04 ± 0.07e	2.20 ± 0.12f	2.10 ± 0.13e	2.24 ± 0.11e
+L + P	6.76 ± 0.02a	5.28 ± 0.08b	5.39 ± 0.07a	5.46 ± 0.06b	5.44 ± 0.13a	5.45 ± 0.11a
+L + Fe + P	4.86 ± 0.03b	4.39 ± 0.10c	4.36 ± 0.02c	3.86 ± 0.43d	4.17 ± 0.10c	4.15 ± 0.10c
Burch soil						
−L − Fe − P	0.18 ± 0.01d	0.29 ± 0.01c	0.30 ± 0.01e	0.24 ± 0.21c	0.33 ± 0.02d	0.38 ± 0.01d
−L + Fe	0.19 ± 0.01d	0.19 ± 0.01c	0.27 ± 0.01e	0.29 ± 0.01c	0.27 ± 0.01d	0.28 ± 0.02d
−L + P	8.24 ± 0.20a	7.06 ± 0.37a	6.33 ± 0.06b	7.53 ± 0.04a	6.99 ± 0.17a	6.63 ± 0.04a
−L + Fe +P	4.24 ± 0.09c	3.56 ± 0.30b	3.59 ± 0.23d	3.92 ± 0.11b	3.77 ± 0.13c	3.50 ± 0.14c
+L − Fe − P	0.31 ± 0.00d	0.31 ± 0.00c	0.32 ± 0.01e	0.38 ± 0.01c	0.37 ± 0.01d	0.38 ± 0.02d
+L +Fe	0.31 ± 0.01d	0.31 ± 0.01c	0.32 ± 0.00e	0.33 ± 0.01c	0.32 ± 0.02d	0.32 ± 0.01d
+L +P	8.05 ± 0.08b	6.95 ± 0.46a	7.12 ± 0.14a	7.28 ± 0.59a	7.00 ± 0.04a	6.48 ± 0.32a
+L + Fe +P	4.19 ± 0.07c	3.87 ± 0.04b	4.11 ± 0.13c	4.02 ± 0.10b	4.01 ± 0.01b	3.93 ± 0.14b

[a]Within columns for each soil, means with a letter in common are not significantly different at the $p < 0.05$ level.

Water-Extractable Arsenic

There was only a slight difference in water-extractable As between the control and the iron-alone treatment for both soils (Figures 1A, Figures 1B). The ($-$lime $+$ P) treatments increased water-extractable As concentrations from trace levels in the untreated Thurmont soil to 36 ± 6.9 and 57 ± 2.2 mg kg^{-1} at 2 and 10 weeks, respectively (Figure 1A). Similarly, at 2 and 10 weeks, the water-extractable As concentration increased from trace to 20 ± 0.61 and 26 ± 0.24 mg kg^{-1} respectively for the ($-$lime $+$ Fe $+$ P) treatment. These two treatments also induced similar increases in the water-extractable As concentrations in the unlimed Burch soil (Fig. 1B). Liming the two soils with the addition of P and Fe, that is, ($+$lime $+$ P) and ($+$lime $+$ Fe $+$ P) treatments, yielded similar increased desorption of arsenate (Figures 2A and Figures 2B). These results suggested that adding phosphate increased the competition between phosphate and arsenate for anion sorption sites (i.e., metal hydroxyl moieties) on soil and organic matter surfaces (Dao 2003). The net result was the increased desorption and buildup of arsenate in the solution phase in ($-$lime $+$ P), ($-$lime $+$ Fe $+$ P), ($+$lime $+$ P), and ($+$lime $+$ Fe $+$ P) treated soils. A positive correlation was found between water-extractable As and P in both soils to support the displacement exchange observed. The linear correlation between the two variables had r^2 values of 0.73 and 0.60 for the Thurmont and Burch soils respectively (Figures 3A and Figures 3B). Peryea (1989) found similar results when lead-arsenate-contaminated orchard soil was leached with P solution.

The ($-$lime $+$ Fe $+$ P) and ($+$lime $+$ Fe $+$ P) treatments also increased water-extractable As concentrations; however, when averaged over the incubation period, these treatments had about 44% less water-extractable As in the soil than the ($-$lime $+$ P) and ($+$lime $+$ P) treatments (Figures 1 and 2). It was postulated that the Fe(OH)$_3$ sorbed and reacted to form insoluble iron phosphates, thereby reducing the solution concentration of phosphate remaining to compete with arsenate for sorption sites. Another possible mechanism for the lower As concentrations of the ($+$Fe $+$ P) treatments included the reaction of Fe with desorbed As to form sparingly soluble iron-arsenate compounds, given the high concentration of added Fe.

The temporal trend in water-extractable As in soil showed an initial rapid increase during 2 and 10 weeks of incubation followed by a slow decline at 16 weeks. One possible explanation for the increase in As desorption may attributed to microbial hydrolysis of organic As forms. Yan-Chu (1994) reported that under aerobic conditions, degradation of As may occur by cleavage of the C-As bond to yield AsO^{3-}. The decline at 16 weeks may indicate the re-adsorption of As on soil and organic matter. In all cases, more As was released from the amended Thurmont soil with the higher organic matter than the Burch soil.
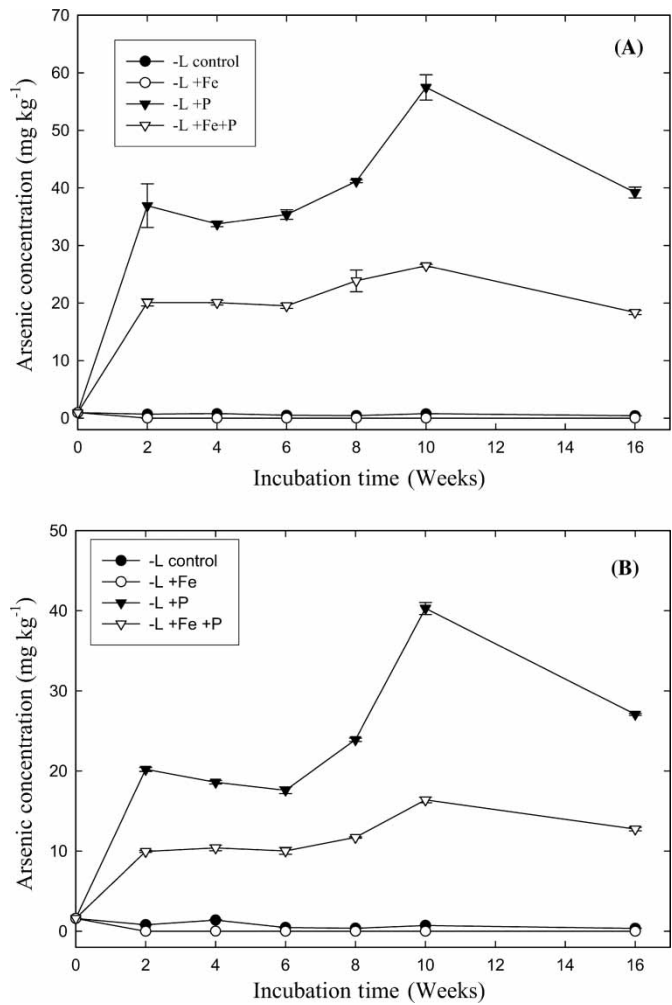
Figure 1. Water-extractable As in unlimed Fe- and P-amended Thurmont (A) and Burch (B) soils during incubation at 26°C. Values are means and standard deviation ($n = 3$ observations).
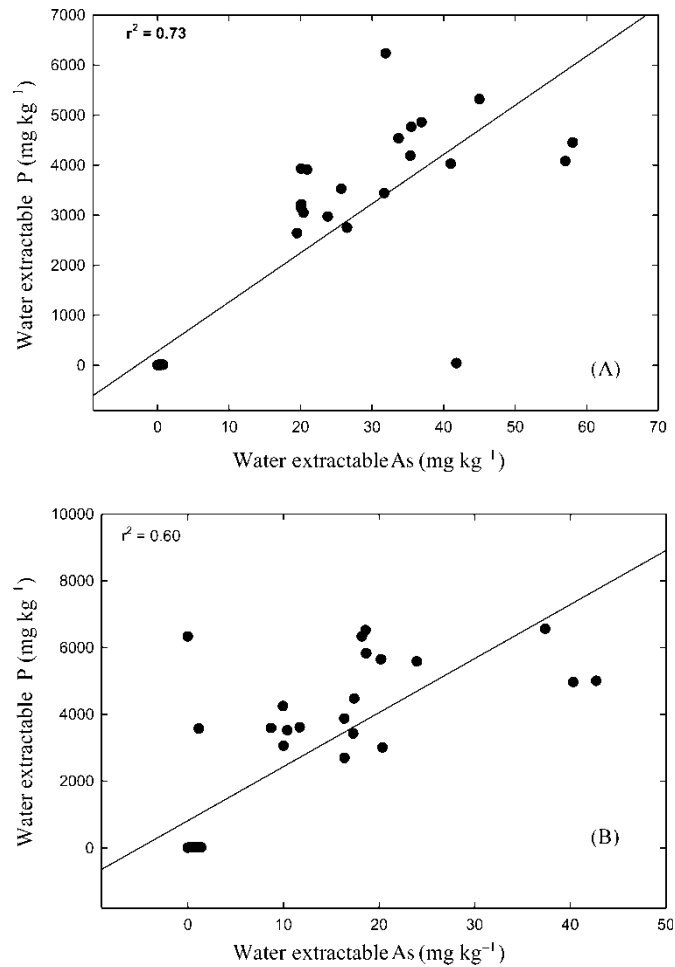
Water-Extractable Lead

Water-extractable Pb concentrations in the Thurmont soil were less than 10.0 mg kg^{-1} for all treatments, with the exception of the (−lime + Fe + P) treatment, in which the Pb concentration increased 20- to 30-fold over untreated soil with time up to 16 weeks (Figure 4A). The addition of P alone, that is, (−lime + P) and (+lime + P) treatments, also increased the Pb concentration in Thurmont soil above the control treatment throughout
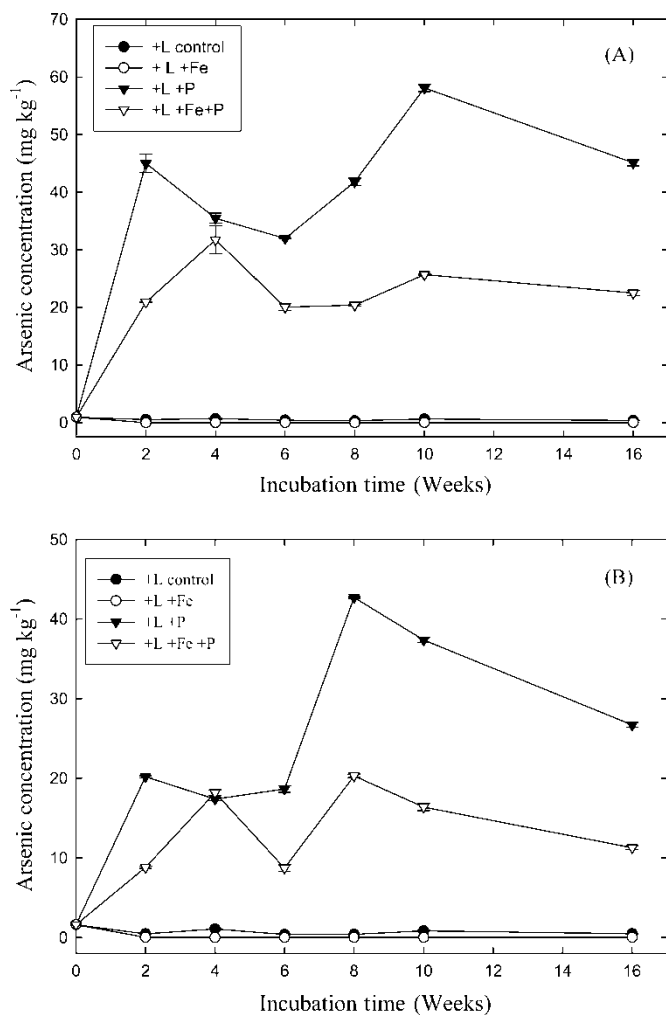
Figure 2. Water-extractable As in limed Fe- and P-amended Thurmont (A) and Burch (B) soils during incubation at 26°C. Values are means and standard deviation ($n = 3$ observations).

the experiment with the highest levels of 9.2 ± 0.23 and 9.8 ± 0.35 mg kg^{-1}, respectively, occurring at 6 weeks (Figures 4A and 5A). Water-extractable Pb concentration in the Burch soil showed a similar trend to that of the Thurmont soil in which there was a linear increase in Pb concentration for the (+Fe + P) treatment during the first 6 weeks (Figures 4A through 5B). The higher water-extractable Pb, concentration observed with the addition of (+Fe + P) treatment may have resulted from interaction of soluble Fe and P in solution to form insoluble iron-phosphate compounds. This

Figure 3. Relationship between water-extractable As and P in unlimed and limed Thurmont (A) and Burch (B) soils during incubation at 26°C.

formation of the iron-phosphate reduces the amount of P available to react with Pb, resulting in higher concentration of extractable Pb in both the Thurmont and Burch soils (Figures 4A through 5B). This was reflected in the strong correlation between Pb and Fe with r^2 values of 0.94 and 0.96 for the Thurmont and Burch soils respectively (Figures 6A and 6B).

Unlike the Thurmont soil, in which the (+P)-induced Pb concentrations remained greater than 3 mg kg^{-1} throughout the incubation, the increased in Pb concentration in the Burch soil with the addition of P decreased over time to the levels of the control (Figures 4B and 5B). The slightly higher Pb concentrations observed in the (+lime + P) treatment of the Burch soil may
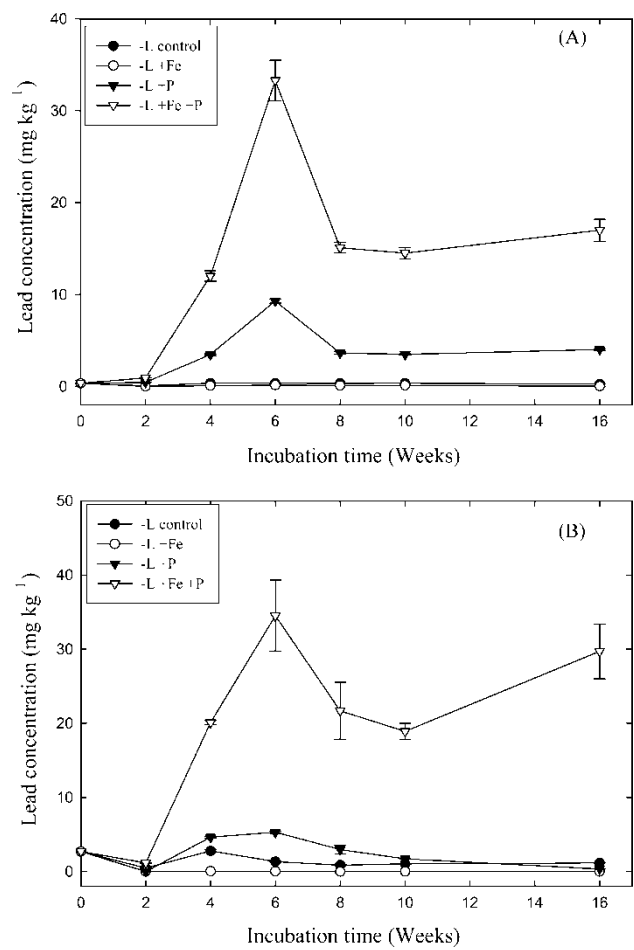
Figure 4. Water-extractable Pb in unlimed Fe- and P-amended Thurmont (A) and Burch (B) soils during incubation at 26°C. Values are means and standard deviation ($n = 3$ observations).

have resulted from the release of Pb from dissolution of organic matter at the higher pH. Sauve, McBride, and Hendershot (1998) reported that the optimum pH for the reduction of Pb solubility is between 5.5 and 6.5. Soil pH greater than 6.5 may induce dissolution of lead phosphate by organic complexation reactions. Turpeinen, Salminen, and Kairesalo (2000) also reported that lime increased the concentration of dissolved organic carbon in the soil. Dissolution of organic matter by $KH_2PO_4^-$ and $Fe(OH)_3$ additions may also contribute to the increased Pb. Sauve, McBride, and Hendershot (1998) reported that dissolved organic matter could enhance metal solubility by forming chelates and maintaining the complexed metals in the solution phase.
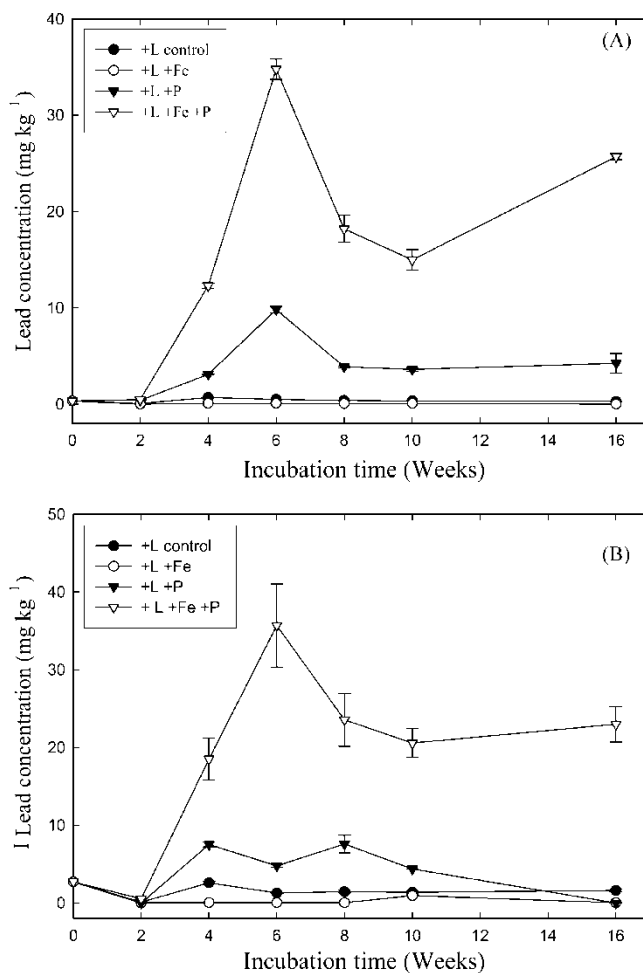
Figure 5. Water-extractable Pb in limed Fe- and P-amended Thurmont (A) and
Burch (B) soils during incubation at 26°C. Values are means and standard deviation
($n = 3$ observations).

The increase in Pb concentration with (Fe and P) addition observed in this
study was not in agreement with the finding of Brown et al. (2004), who found
reduction in Pb concentration with Fe and P application. The differences
between the two experiments may have resulted from the type of phosphate
and iron used. Brown et al. (2004) used triple superphosphate and an iron-
rich residue, whereas in the present experiment potassium phosphate and
$Fe(OH)_3$ were used.

The increase in water-extractable Pb observed in this experiment with
the addition of lime, potassium phosphate, and iron to lead-arsenate-
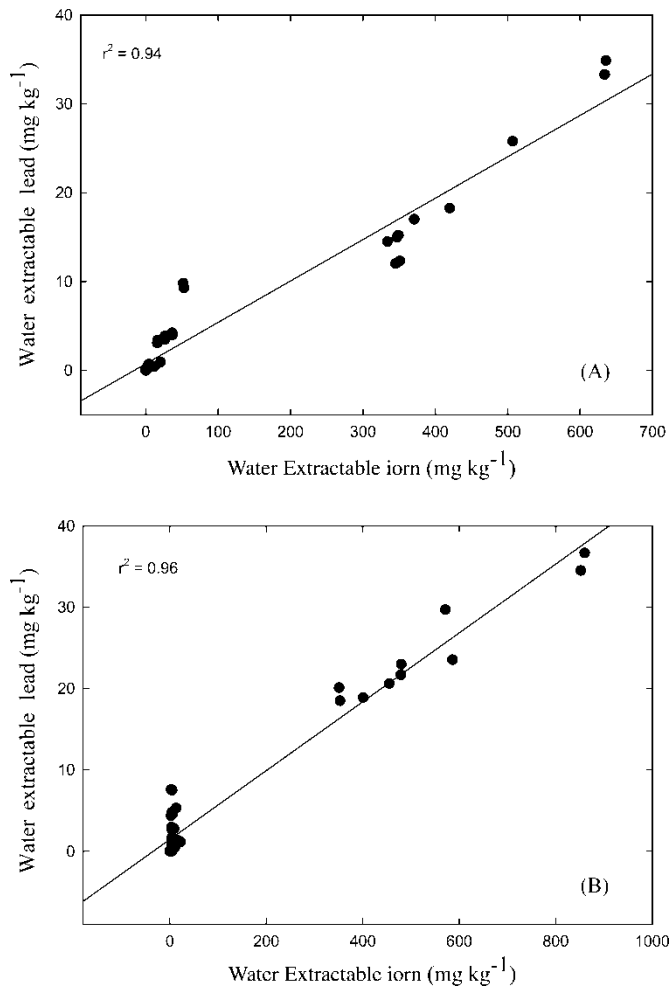
Figure 6. Relationship between water-extractable Fe and Pb in unlimed and limed
Thurmont (A) and Burch (B) soils during incubation at 26°C.

contaminated soils demonstrated that soluble Pb in the surface soil could
potentially increase the Pb levels in runoff and transported to surface
waters and sediment. Sauve, McBride, and Hendershot (1998) concluded
that remediation of Pb with phosphate may limit Pb toxicity but did not
completely immobilize Pb.

Wang and Benoit (1996) found that soluble Pb released from the surface
soil was re-immobilized through the absorption of ionic Pb^{2+} or organic Pb
colloids by subsurface layers reducing the amount of Pb reaching the
ground water.

CONCLUSION

Potential loss of agricultural lands in fruit tree production to urbanization and change in land use brought forth the importance of developing *in situ* remediation practices for lead-arsenate-contaminated soils. Addition of lime, phosphate-phosphorus, and $Fe(OH)_3$ to soils collected from two active orchards showed that P application at the rate of 43.9 g KH_2PO_4 kg^{-1} to lead-arsenate-contaminated soils increased the release of water-extractable As and Pb. The highly soluble source of phosphate also decreased the efficacy of the Fe additive in reducing soluble As in these high-arsenate soils. Arsenic levels were more than 10 mg kg^{-1} in both soils, which is greater than the 10 µg As L^{-1} USEPA drinking water limit. The increased in Pb levels with lime, Fe, and P application demonstrated that the addition of lime, potassium phosphate, and iron to these lead-arsenate-contaminated soils could increase water-extractable Pb concentration beyond that of the unamended soil. The results from this experiment suggested that the solubility of As and Pb were controlled not only by pH, Fe, and P but also possibly by organic matter and soil microbes. Further investigation will be needed to determine the long-term effects of these amendments on the sequestration of Pb and As in lead-arsenate soils and to quantify the relative importance of dissolved carbon in the solubilization of As and Pb.

ACKNOWLEDGMENTS

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